Enabling Extreme Fast Charging Through Anode Modification

Esther Takeuchi
Stony Brook University
6/3/2020
Collaborators: David Bock (BNL), Amy Marschilok (SBU), Kenneth Takeuchi (SBU)

This presentation does not contain any proprietary, confidential, or otherwise restricted information

BROOKHAVEN NATIONAL LABORATORY

Project ID: bat396

Stony Brook University

Overview

Timeline

- Project start date: Jul. 2018
- Project end date: Aug. 2020
- Percent Complete: 80%

Budget

- Total project funding:
  - DOE share: $800,000
  - Cost share: $92,496
- Funding for FY 2020: $400,000

Barriers

- Barriers addressed:
  - The major barrier preventing extreme fast charging of Li-ion batteries is Li plating at the graphite anode.

Partners

- Collaboration: Stony Brook University (SBU) and Brookhaven National Laboratory
- Project Lead: SBU

Relevance

Project Goal

- Enable extreme fast charging by changing the overpotential for lithium deposition at the graphite surface through electrode surface treatment with nanometer scale Cu or Ni films.

Impacts

- Surface coatings on a graphite electrode will increase the overpotential for Li nucleation and growth, thus suppressing Li deposition at high charge rates.
- By mitigating Li plating, the battery will address the EERE goal of achieving 500 6C charge/ 1C discharge cycles with less than 20% fade in specific energy delivered from fast charge protocol.
- Deliberate increase of Li deposition overpotential is a new concept – the program represents a potentially transformative strategy for Li plating suppression compatible with current manufacturing methods.

Objectives

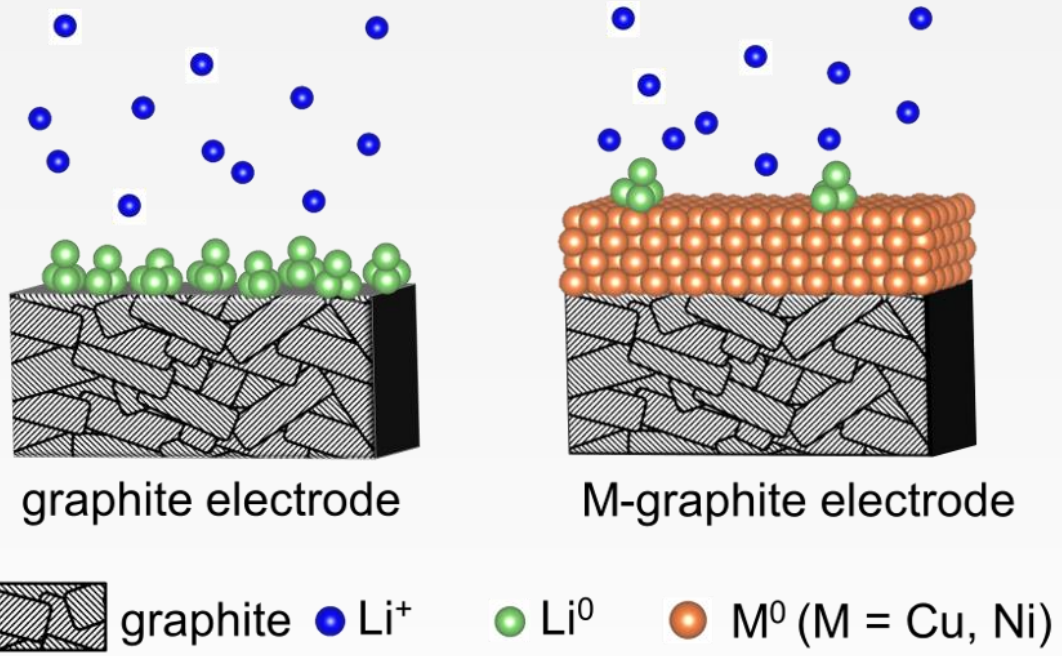
1: Prepare and characterize graphite electrodes coated with nanometer scale Ni or Cu layers.
2: Perform electrochemical evaluation of Ni-graphite and Cu-graphite electrodes in half and full cell configurations.
3: Improve cell rate capability and cycle life through optimization of metal coating type and thickness.
4: Evaluate extreme fast charging capability of cells containing metal coated graphite electrodes and benchmark against cells using uncoated graphite electrodes.

Milestones for FY20

Quarter	Milestone	Status
Q5	Preparation and characterization of nm scale metal coated graphite electrodes at different thicknesses	Complete
Q6	Optimization of metal coating type and thickness in full cell configuratio	Complete
Q7	Identification of nm scale metal coated electrode with optimum cycling performance at 6C rate	Complete
Q8	Demonstration of metal coated electrode with capacity retention at 10 minute charge rate > uncoated (control) electrode	In progress
Q8	2 Ah cells incorporating final fast charge technology provided to DOE	In progress

Approach

- **Concept:** graphite electrodes coated with nanometer scale layers of Ni or Cu metal



- A free energy barrier must be overcome for the formation of Li nuclei on the electrode surface

Electrocrystallization overpotential: $\eta = \eta_n + \eta_p$

η_n : nucleation overpotential – initial nucleation of Li

η_p : plateau overpotential –growth on existing nuclei

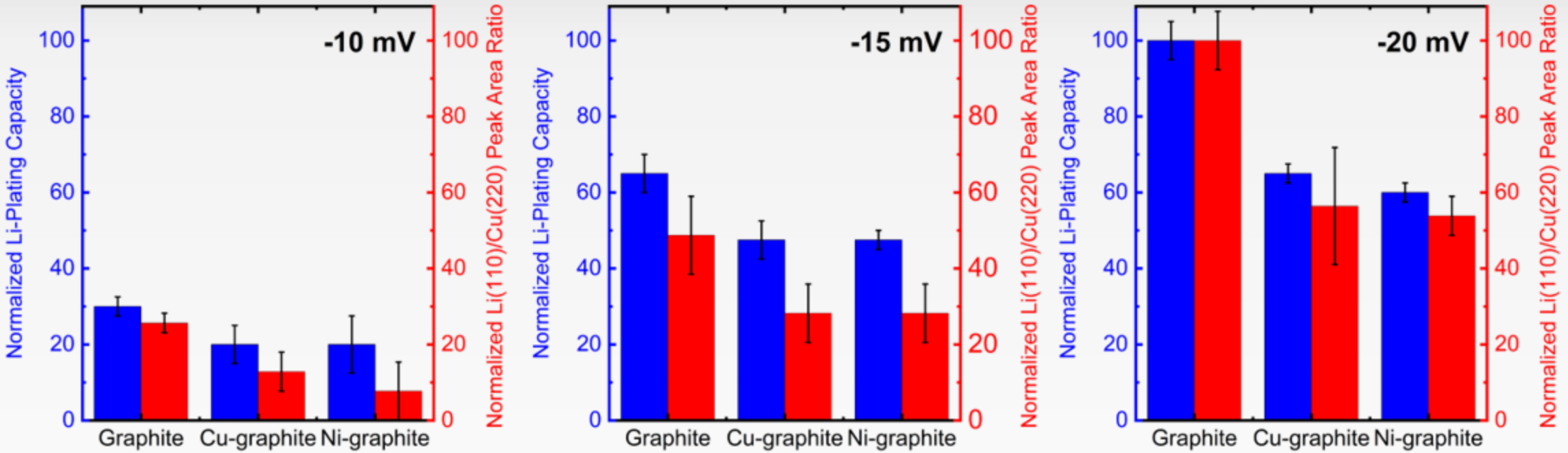
- Cu and Ni (FCC) have dissimilar crystal structures to Li (BCC) and no phase solubility
- Deliberate modification of the graphite substrate with Cu or Ni will increase the overpotential for Li nucleation, inhibiting Li plating at high charge rates

Benefits of Approach

- Suppression of Li deposition through overpotential control
- Nanoscale coatings preserve energy density
- Can be integrated with state-of-the-art anodes

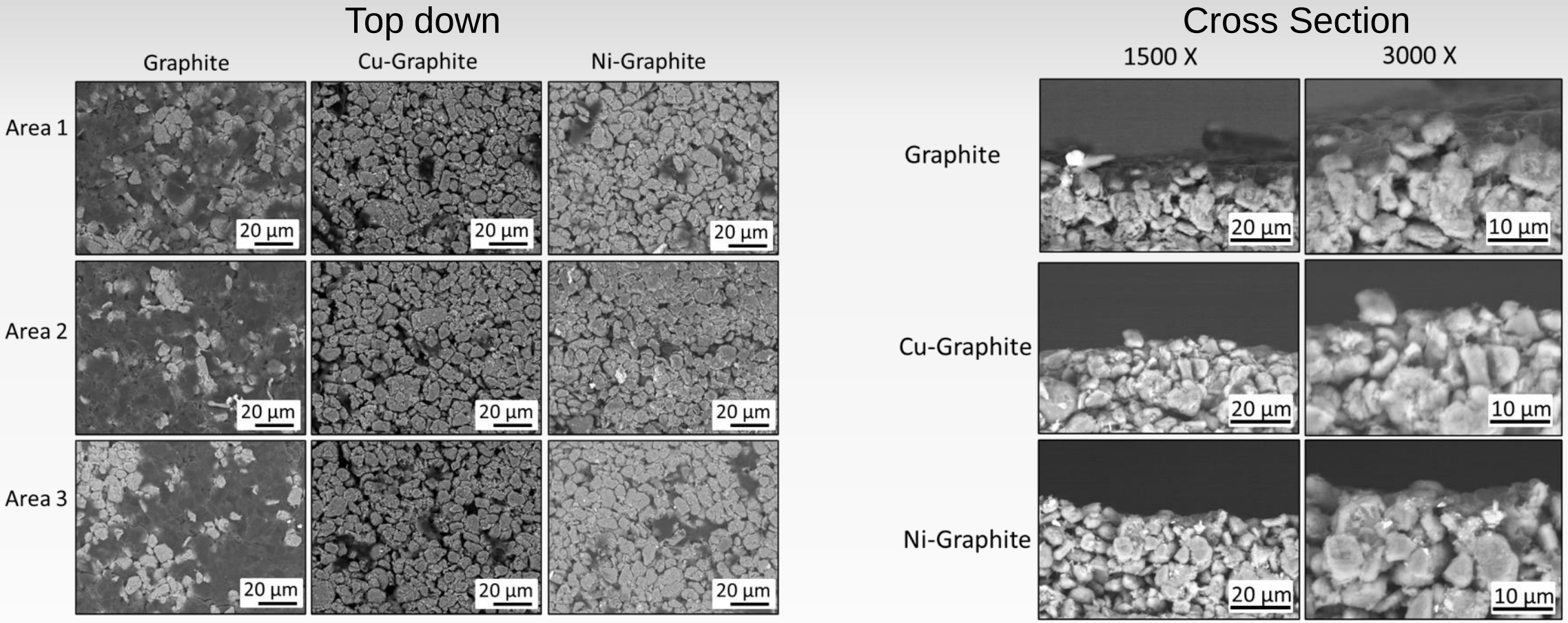
Technical Accomplishment – Li Plating Quantification on Graphite, Cu-graphite, Ni-graphite by XRD

Normalized Li Plating Capacity and Normalized Li(110) XRD Peak Area



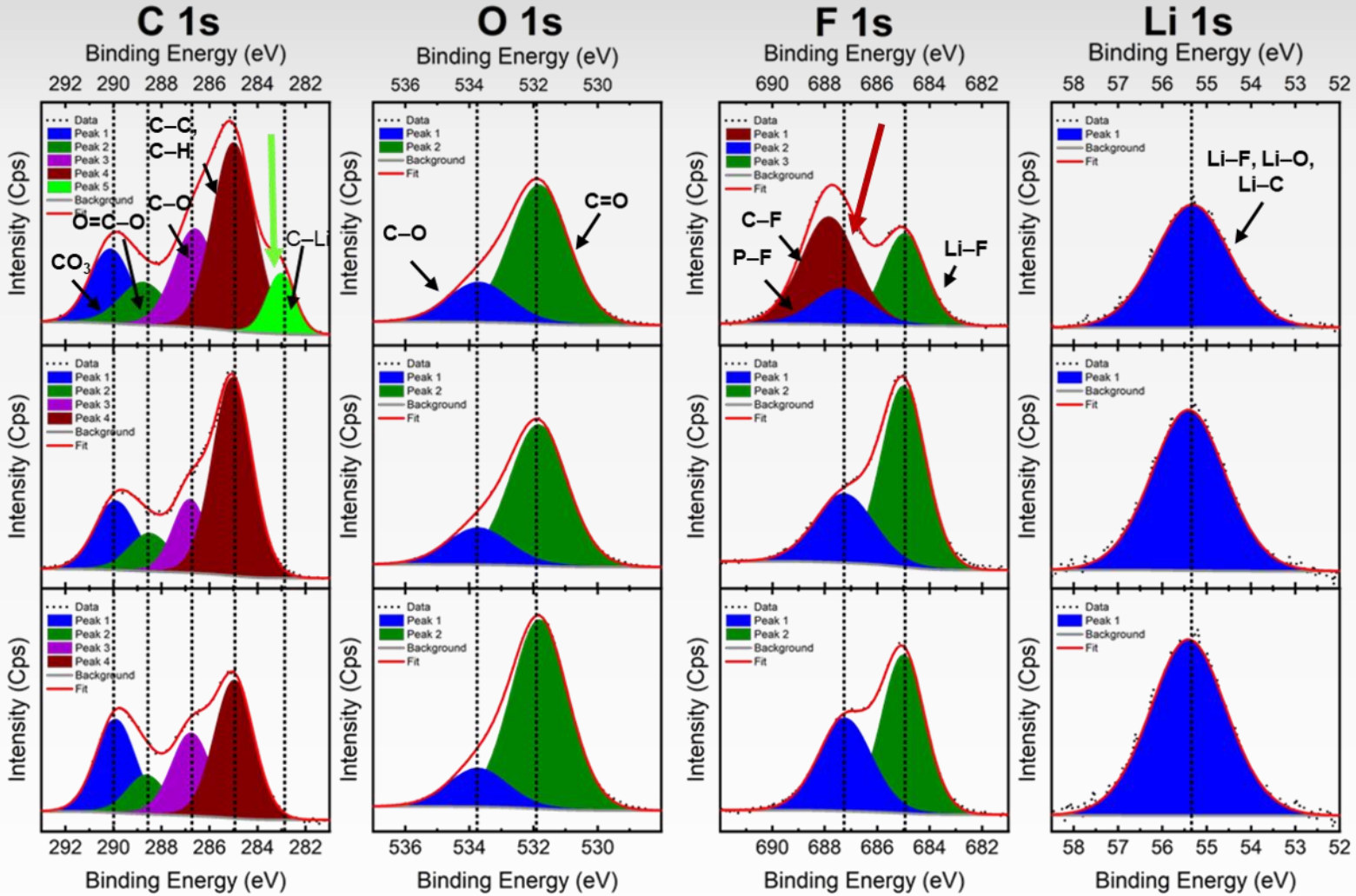
- Li-plating capacities for metal coated electrodes are 30-40% lower than the uncoated graphite plating capacity at each voltage hold
- The Li^0 (110) peak areas normalized against Cu foil (220) peak areas for the Cu or Ni coated electrodes are < 50% of the control graphite electrode at each condition

Technical Accomplishment – Li Plating on Graphite, Cu-graphite, Ni-graphite by SEM



- Similar morphology of Li deposits is observed, but concentration is lower on Cu-graphite, Ni-graphite
- Cross-sectional images indicate that the plated Li is contained to the upper layers of the graphite electrode, extending down ~ 10 µm

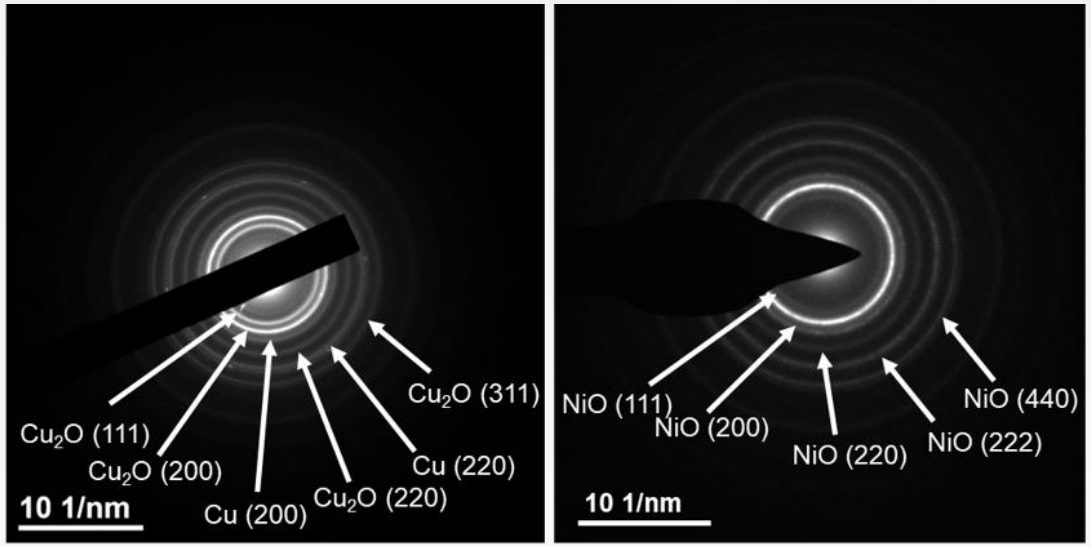
Technical Accomplishment – Solid Electrolyte Interphase Characterization: XPS of graphite, Cu-graphite, Ni-graphite



- XPS spectra of electrodes after formation cycling indicate very similar surface species where the metal coating is not altering the surface chemistry of the SEI
- C1s peak assigned to LiC and F1s peak assigned to PVDF are not observed for the two metal coated samples due to the photoelectron escape depth < 10 nm.

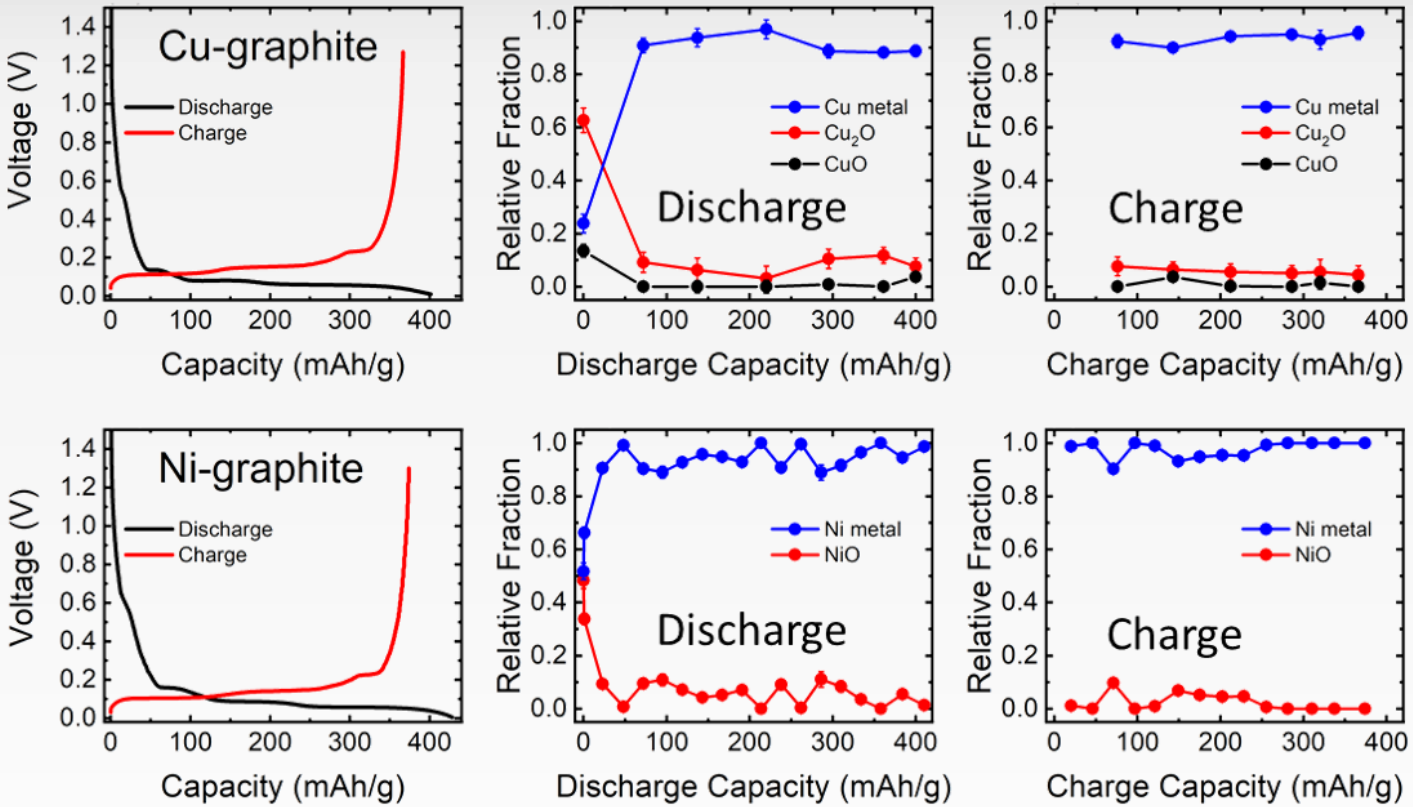
Technical Accomplishment – Characterization of Metal Film Oxidation State

Selected Area Electron Diffraction



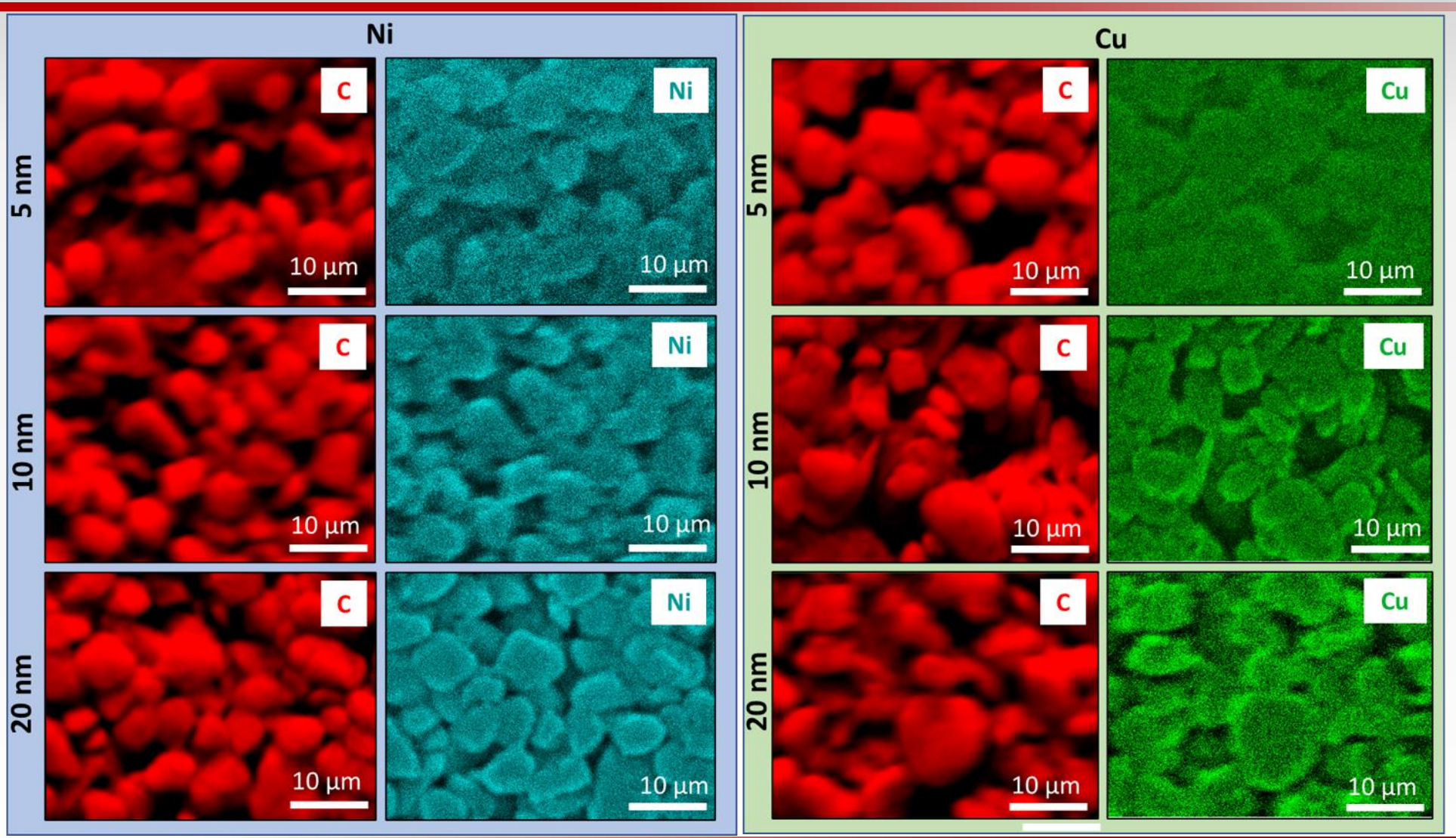
- Pristine sputtered films are initially oxidized

Operando XANES



Cu and Ni films are electrochemically reduced to Cu and Ni metal during lithiation and do not re-oxidize under negative electrode voltages – Cu_2O to Cu: 4.2 µAh/cm^2; NiO to Ni 4.8: µAh/cm^2

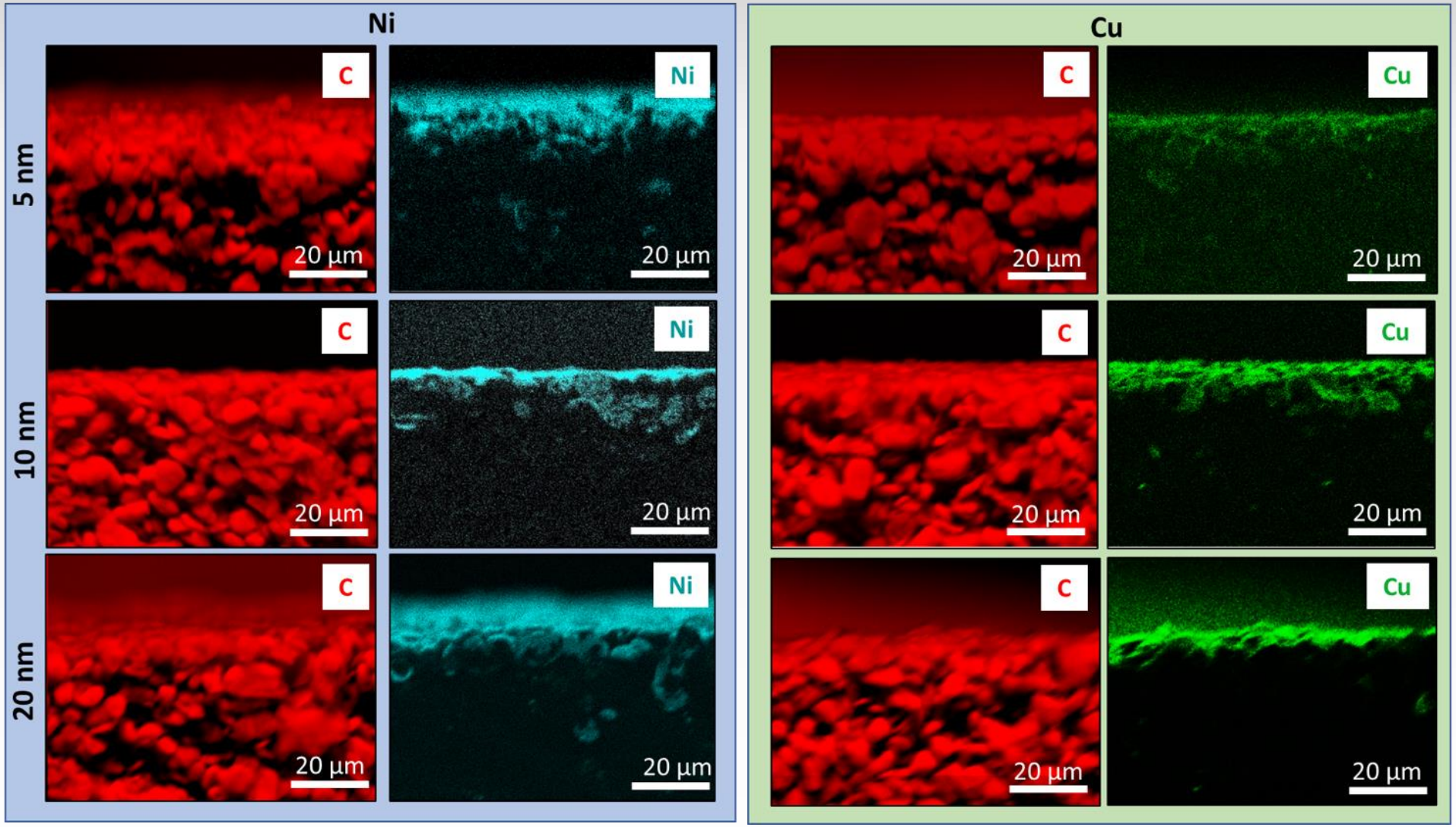
Technical Accomplishment – Preparation and Characterization of nm scale metal coated electrodes at different thicknesses – EDS Mapping



Film coverage on graphite does not change as a function of thickness

Target thickness	AFM Measured Thickness (nm)	
	Cu	Ni
5 nm	5.3 ± 0.8	5.0 ± 0.5
10 nm	10.2 ± 0.5	9.6 ± 0.8
20 nm	19.9 ± 0.6	19.5 ± 0.8

Technical Accomplishment – Preparation and Characterization of nm scale metal coated electrodes at different thicknesses – EDS Mapping

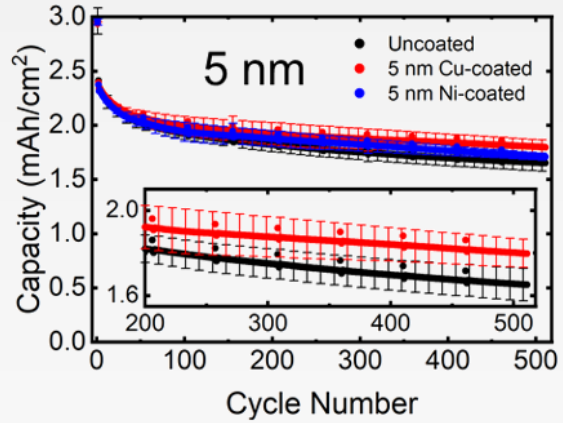


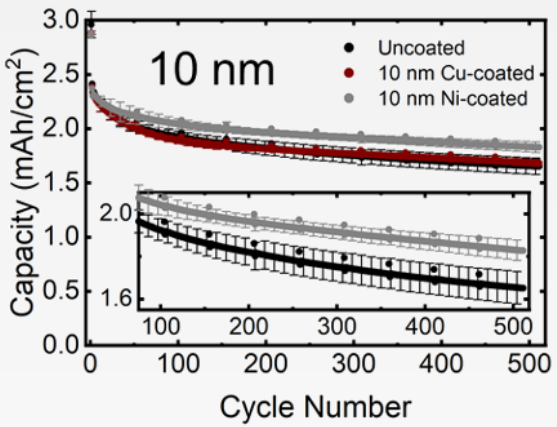
Cross-section analysis shows that surface films are concentrated at the upper surface of the graphite electrode

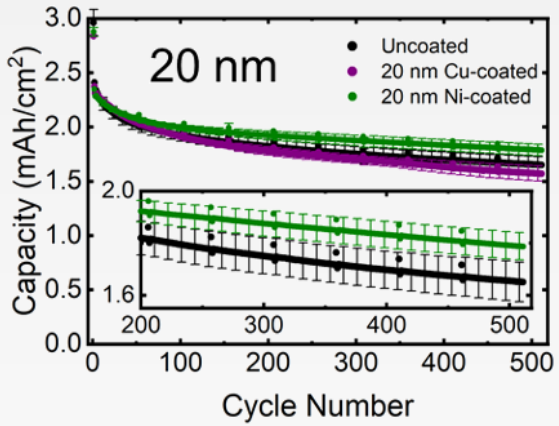
Technical Accomplishment – Optimization of Metal Coating Type and Thickness

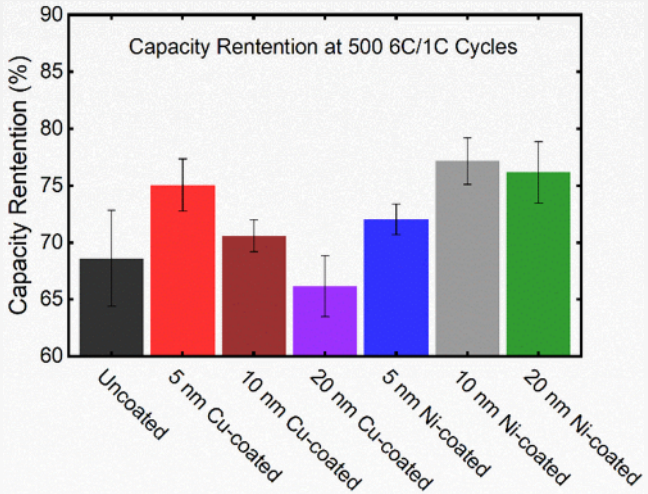
10 minute charge (6C CC, CV at 4.3 V), 1C discharge, C/3 discharge every 50 cycles

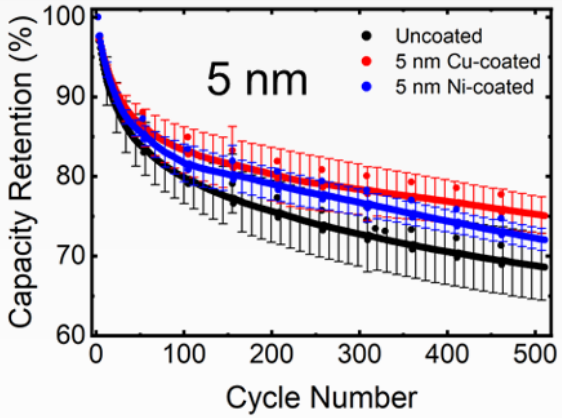
- Anode: 90% graphite, 3% carbon black, 7% PVDF
- Cathode: 90% 622NMC, 5% carbon black, 5% PVDF
- Electrolyte = 1M $LiPF_6$ 30:70 EC:DMC + 2% VC

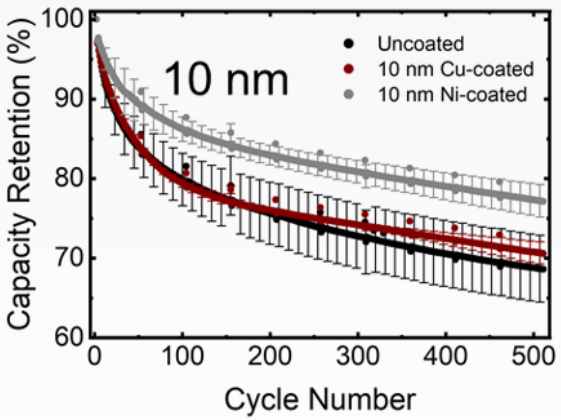


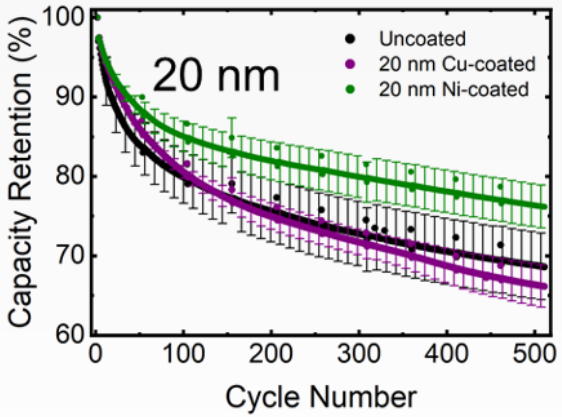






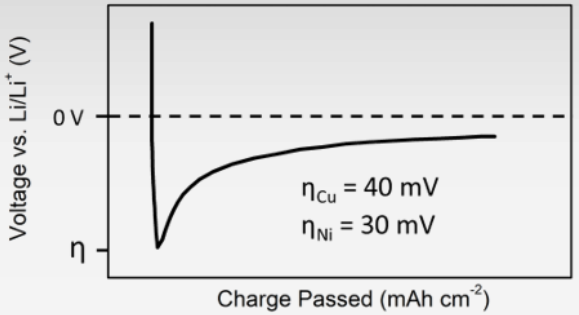




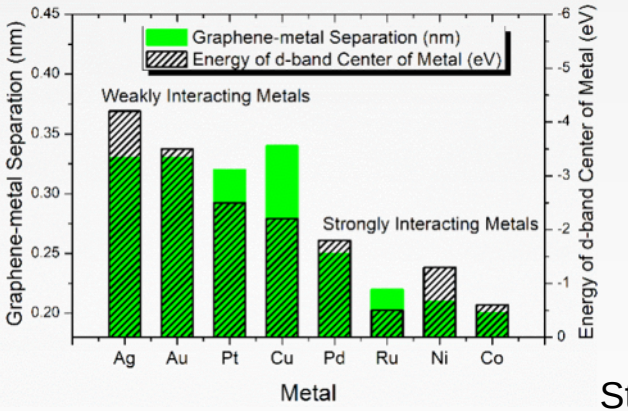


Metal coating type and thickness with 10 nm Ni identified as the metal coated electrode with highest capacity retention at 6C rate (Q6, Q7 milestones)

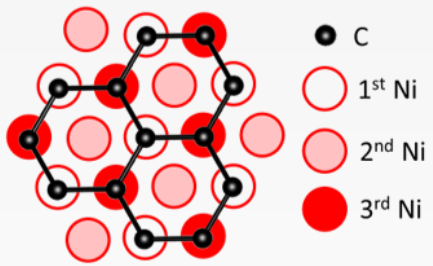
M-Carbon Interactions



Overpotentials for Li deposition on Ni and Cu[1]



Correlation of graphene-metal separation with the energy of TM d-band center[5]



Structure of graphene-Ni(111) determined from LEED[7]

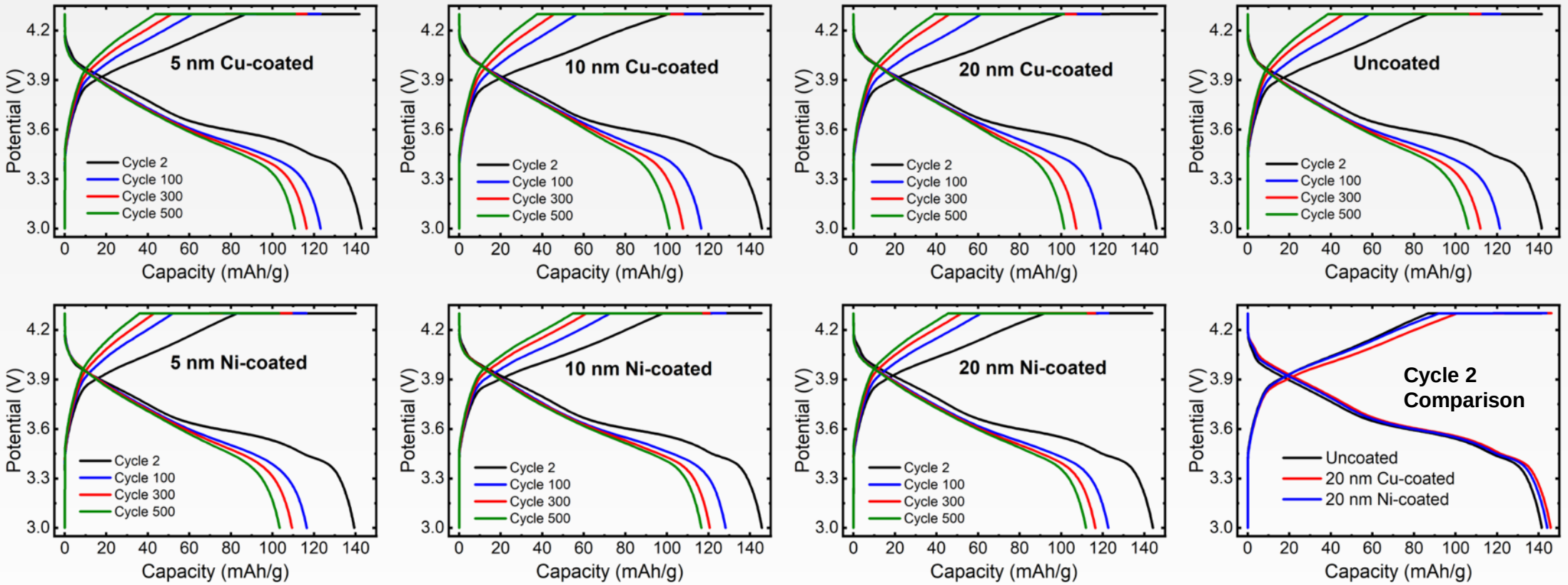
- Both Cu and Ni metal foils show high overpotentials for Li deposition[1], but experimental results show Ni coatings are more effective at reducing capacity fade compared to Cu
- Compared with metal foils, properties of Ni and Cu sputtered on carbon are affected by M-carbon interaction
- M-carbon interaction strength is predicted to be higher for Ni compared to Cu based on lattice matching and electronic structure:
  - M(111) surfaces dominate crystallographic textures from sputtering deposition of Cu and Ni[2,3]
  - Ni(111) is better lattice matched with graphene than Cu(111) (~1.2% vs ~4.0%)[4,5]
  - d-band center correlates to extent of filling of (M3*d*–O2*p*) antibonding states
  - Lower d-band of Cu results in increased filling of antibonding states relative to Ni (destabilizes the M-C bond) [6]
- Weaker M-C interaction for Cu-coated electrodes may cause metal film physical instability during cycling, reducing effectiveness

[1] Yan, K.; Lu, Z.; Lee, H.-W.; Xiong, F.; Hsu, P.-C.; Li, Y.; Zhao, J.; Chu, S.; Cui, Y., *Nat. Energy* **2016,** *1* (3), 16010. [2] Kim, J.; Wen, S.; Jung, D.; Johnson, R., *IBM journal of research and development* **1984,** *28* (6), 697-710; [3] Mitra, R.; Hoffman, R.; Madan, A.; Weertman, J., *J. Mater. Res.* **2001,** *16* (4), 1010-1027; [4] Batzill, M. *Surf. Sci. Rep.* **2012,** *67* (3-4), 83-115; [5] Dahal, A.; Batzill, M. *Nanoscale* **2014,** *6* (5), 2548-2562; [6] Hammer, B.; Norskov, J. K. *Nature* **1995**, *376*, 238-240; [7] Gamo, Y.; Nagashima, A.; Wakabayashi, M.; Terai, M.; Oshima, C. *Surface Science* **1997**, *374*, 61-64.

Technical Accomplishment – Optimization of Metal Coating Type and Thickness

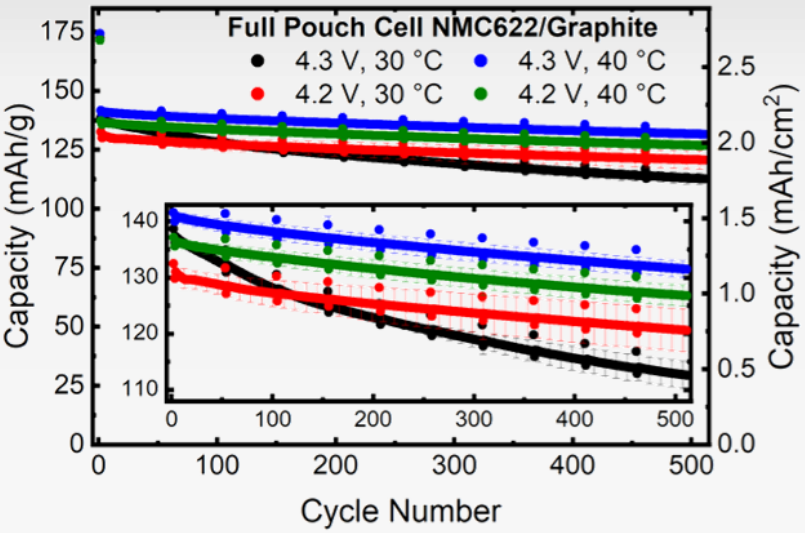
10 minute charge (6C CC, CV at 4.3 V), 1C discharge, C/3 discharge every 50 cycles

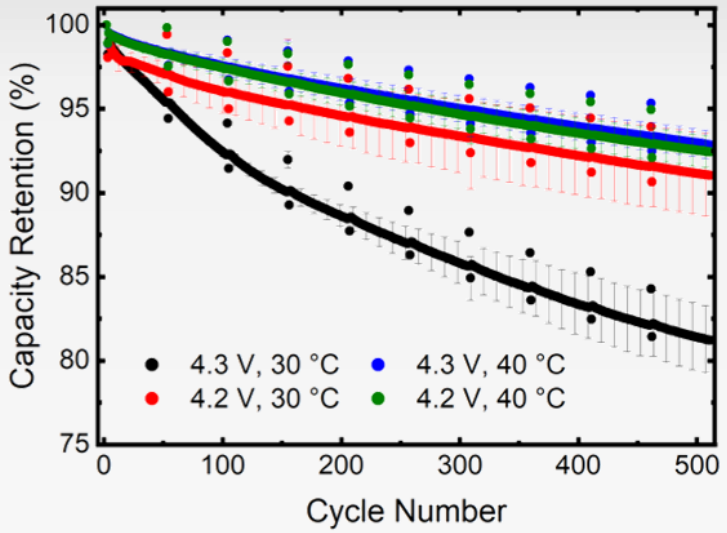
- Anode: 90% graphite, 3% carbon black, 7% PVDF
- Cathode: 90% 622NMC, 5% carbon black, 5% PVDF
- Electrolyte = 1M $LiPF_6$ 30:70 EC:DMC + 2% VC



- No significant differences in the voltage profiles are observed for the various metal coating types/thicknesses.

Technical Accomplishment – Optimization of Charge Protocol (voltage limit, temperature)

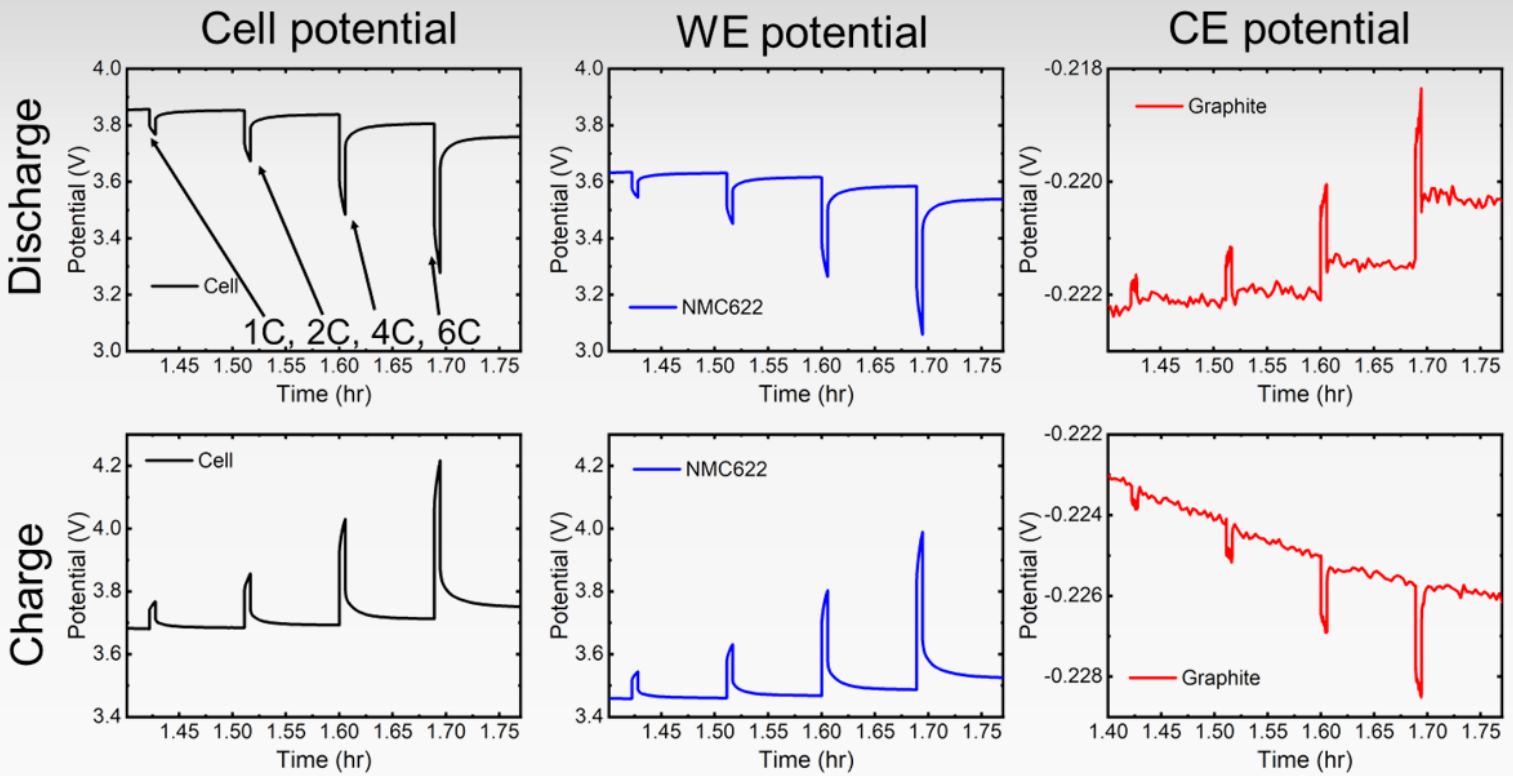




Condition	Areal Capacity (mAh/cm²)		Capacity Retention (%)
	Cycle 2	Cycle 500	
30°C, 4.2 V	2.12 ± 0.04	1.93 ± 0.06	91 ± 3
30°C, 4.3 V	2.21 ± 0.04	1.80 ± 0.07	81 ± 2
40°C, 4.2 V	2.13 ± 0.03	1.97 ± 0.05	93 ± 1
40°C, 4.3 V	2.26 ± 0.04	2.10 ± 0.02	93 ± 1

- Testing conditions were optimized by evaluating upper voltage limit (4.2 V vs. 4.3 V) and operating temperature (30°C vs. 40°C) using a 2 x 2 designed experiment matrix
- A 10 minute charge and 5C CC discharge was used for all conditions tested
- 4.3 V limit at 40 °C offers the the highest delivered capacity and capacity retention under fast charge

Technical Accomplishment – Determine Polarization Under XFC



- High current interval testing of 3-electrode pouch cells with NMC622 cathode and graphite anode reveal polarization under 1C to 6C charge and discharge (20 s duration)
- Tests including longer current intervals with surface treated anodes will be conducted

Pulse Data at 50% SOC

Rate	R_{DC} (Ω)			$\Delta V_{Graphite}$ (mV)
	Cell	NMC622	Graphite	
1C (discharge)	4.46	4.44	0.02	0.6
2C (discharge)	4.45	4.43	0.02	0.9
4C (discharge)	4.38	4.35	0.03	2.1
6C (discharge)	4.36	4.34	0.02	3.0
1C (charge)	4.31	4.28	0.03	0.5
2C (charge)	4.28	4.25	0.02	1.0
4C (charge)	4.18	4.16	0.02	1.9
6C (charge)	4.17	4.15	0.02	2.7

Responses to Previous Year Reviewers Comments

- A reviewer commented that because electrolyte still penetrates into the electrode, Li-metal will plate inside the electrode:

  -Cross-sectional SEM images of anodes indicate that the plated Li is limited to the upper layer of the graphite electrode, but does extend into the electrode ca. 10 µm (Slide 7).

- Reviewers commented that it is unclear if metal coatings will affect discharge power:

  -Voltage profiles of the metal coated electrodes during 1C discharge indicate that the metal coatings do not increase electrode polarization (Slide 14) .

- A reviewer commented that the effect of the graphite-metal interface on the SEI needs to be studied:

  -XPS of cycled anodes indicate very similar surface species where the metal coating is not altering the surface chemistry of the SEI (Slide 8).

- A reviewer commented that determination of the overpotentials for Li deposition is needed:

  -3-electrode cells were developed to quantify the magnitude of the overpotential for control graphite anodes (Slide 16). Additional tests with surface treated anodes will be conducted.

Collaborations; Remaining Challenges and Barriers

Collaborations

- User proposal systems actively used for interaction with Brookhaven National Laboratory (National Synchrotron Light Source II, Center for Functional Nanomaterials) for metal film deposition and characterization.
- Brookhaven National Laboratory Leads Cell Characterization Efforts
- Computational efforts underway at NREL by Kandler Smith

Remaining Challenges and Barriers

- Evaluate overpotential of surface treated vs. control anodes as a function of charge rate
- Identify cause of differences in capacity retention for Cu-coated electrodes vs. Ni-coated electrodes
- Evaluate fast charging capability vs. control cells using optimized fast charge protocol

On-going and Proposed Future Research (FY20)

- **Q8 Milestone:** Demonstrate metal coated electrode with capacity retention at 10 minute charge rate > uncoated (control) electrode; use optimized fast charge protocol
- **Q8 Milestone:** Provide 2 Ah cells incorporating final fast charge technology to DOE

- Test 3-electrode cells with Ni-graphite and Cu-graphite negative electrodes to evaluate polarization vs. control graphite electrode under charge and discharge
- Complete Li-plating investigations of Ni-graphite and Cu-graphite under different conditions (surface film thicknesses, anode polarization voltages)
- SEM and EDS mapping of electrodes after extended cycling under 10 minute charge rate to evaluate uniformity of metal coatings: literature suggests stronger interaction of graphite surfaces with Ni vs. Cu

Any proposed work is subject to change based on funding levels

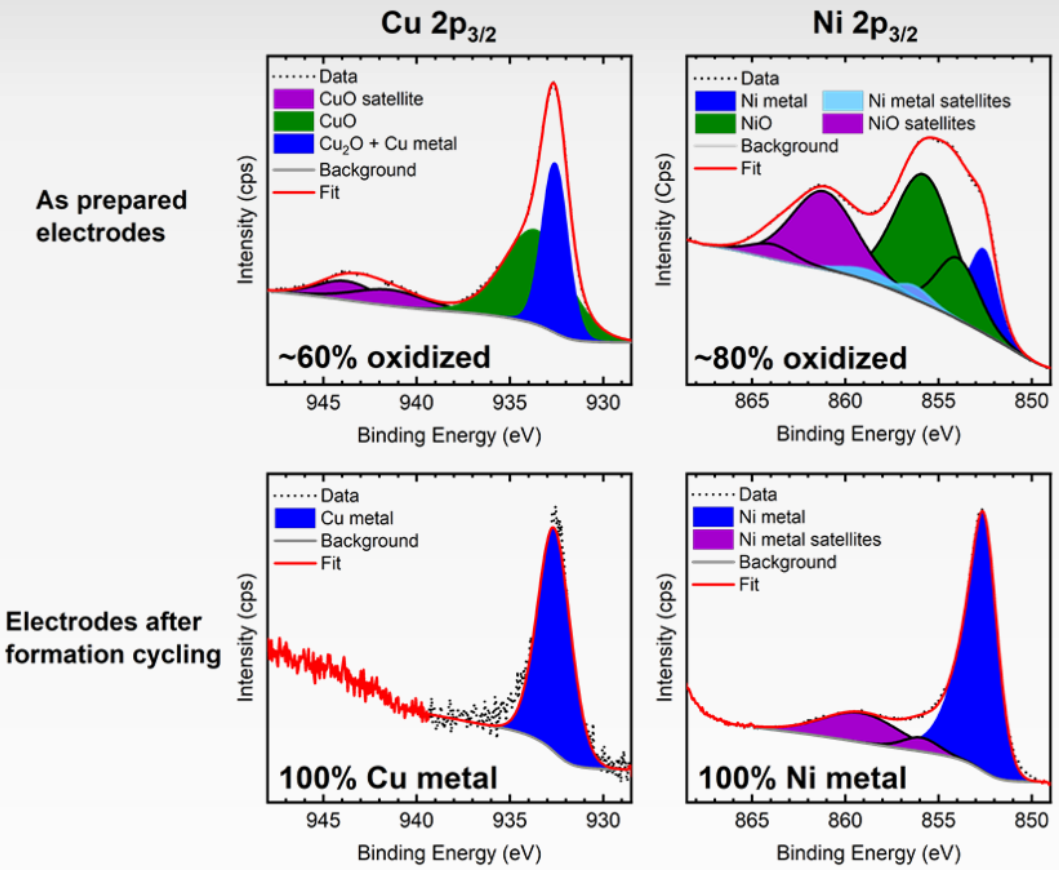
Summary

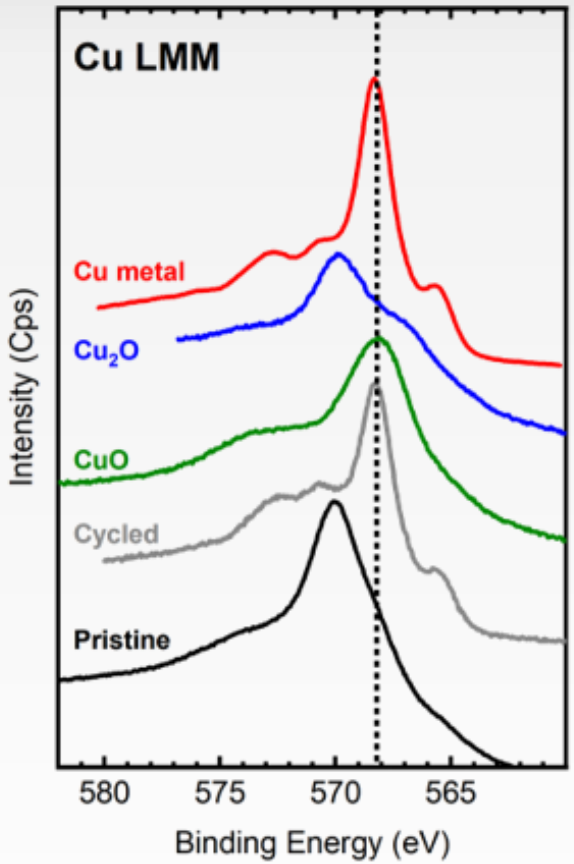
Program is on schedule.

- Demonstrated single layer full cells with Ni-graphite anodes show reduced capacity fading and reduced Li deposition on recovered electrodes under 10 minute charge rate
- Li plating deposition experiments show reduced Li plating on surface treated graphite compared to untreated graphite electrodes
- XPS characterization of electrodes post-cycling indicates that surface treatment does not impact SEI composition
- Graphite electrodes sputtered with 5, 10, and 20 nm Cu and Ni and characterized by AFM, SEM, EDS to affirm nature of coating
- Tested 5, 10, and 20 nm Cu and Ni coated anodes under 10 minute charge: down selected 10 nm Ni-graphite electrodes as optimum for 2 Ah cell build
- Pulse testing of 3-electrode pouch cells with NMC622 cathode and control graphite anode demonstrate the relative amount of polarization under 1C to 6C charge and discharge
- Charge protocol for 2 Ah pouch cells has been optimized

Technical Backup Slides

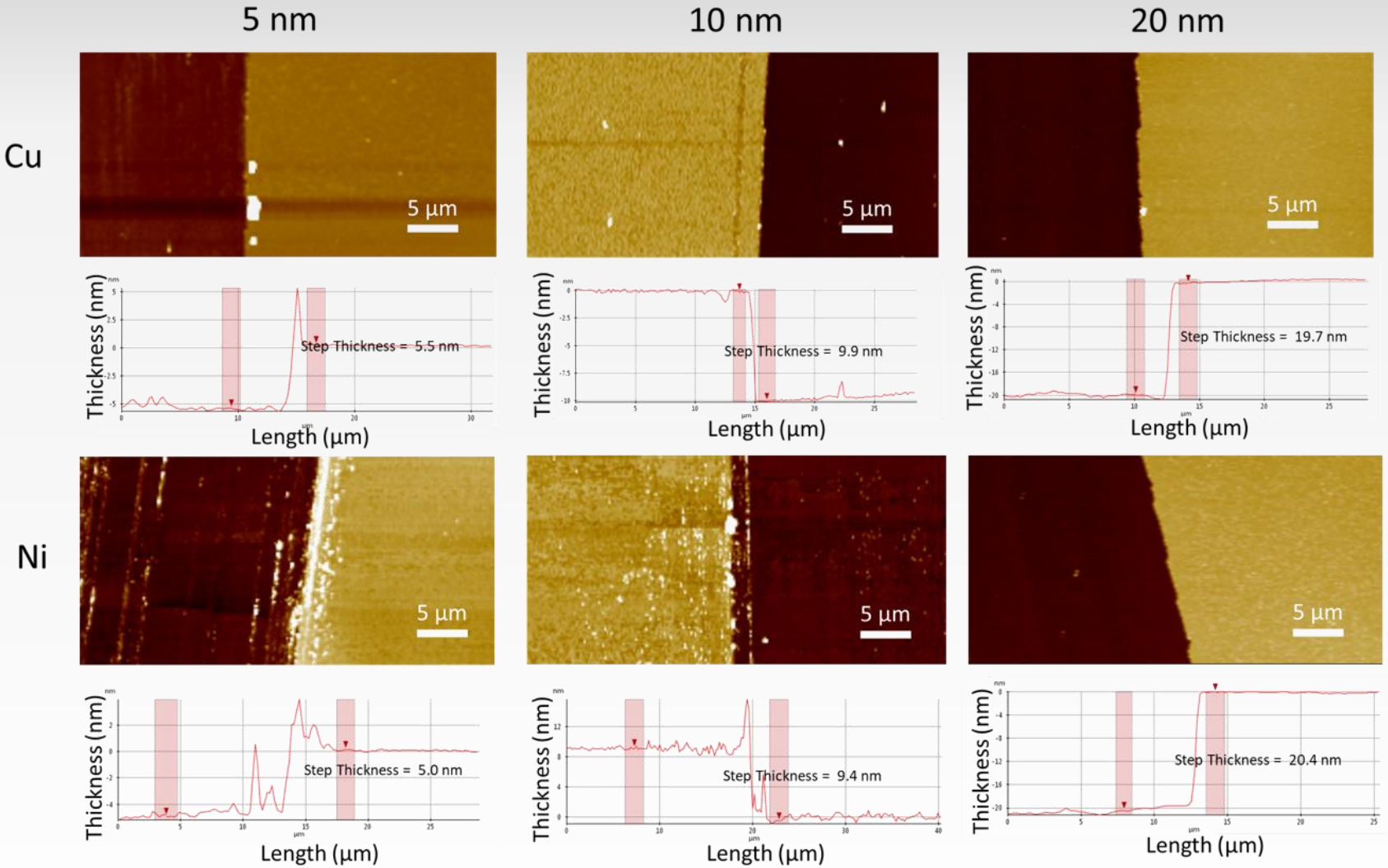
Technical Accomplishment – Metal Film Characterization: XPS of pristine and cycled graphite, Cu-graphite, Ni-graphite





- Initial metal films are oxidized on air exposure. XPS indicates that after formation cycling Cu and Ni films are electrochemically reduced to Cu metal and Ni metal, and do not re-oxidize during delithiation of graphite.
- Contribution of reduction of oxide films to irreversible capacity of electrode is negligible:
  Cu_2O to Cu: 4.2 μAh/cm^2
  NiO to Ni 4.8 μAh/cm^2

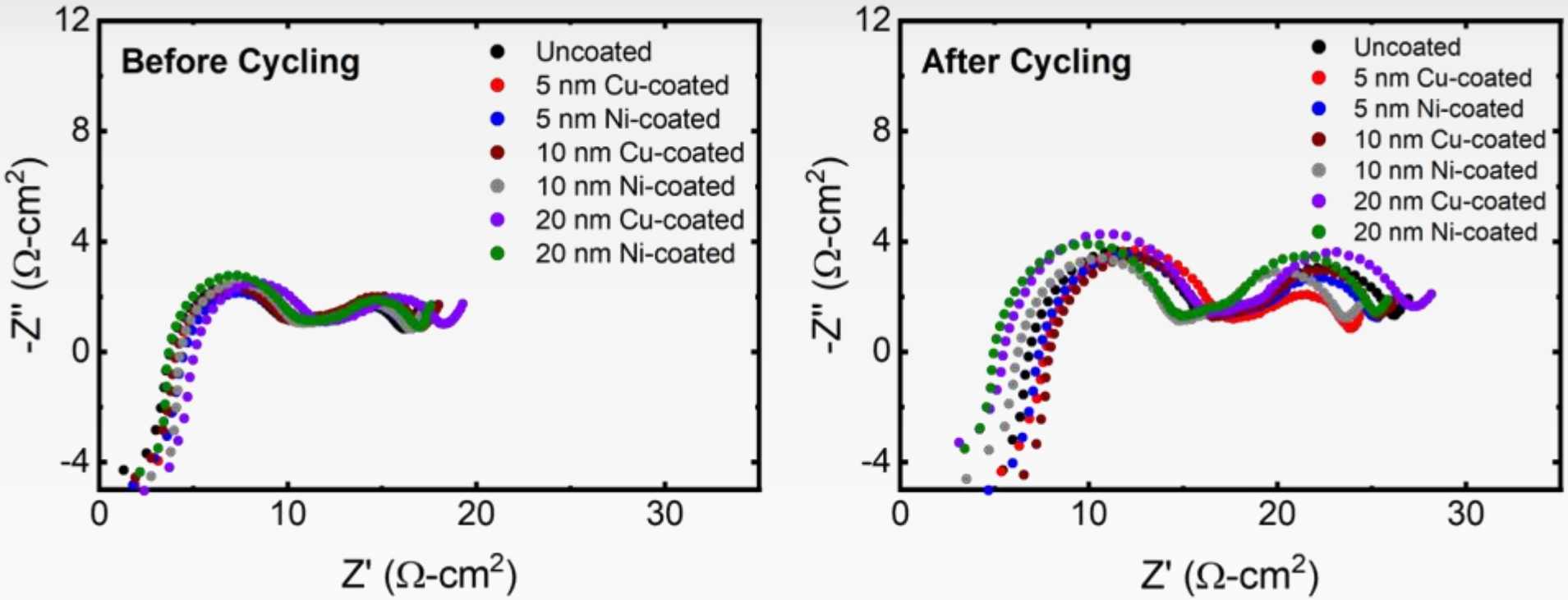
Technical Accomplishment – Preparation and Characterization of nm scale metal coated electrodes at different thicknesses – AFM



- Thicknesses of the deposited Ni and Cu films were verified via non-contact atomic force microscopy (AFM) analyses of ultra-flat SiO_2 wafers

Target thickness	AFM Measured Thickness (nm)	
	Cu	Ni
5 nm	5.3 ± 0.8	5.0 ± 0.5
10 nm	10.2 ± 0.5	9.6 ± 0.8
20 nm	19.9 ± 0.6	19.5 ± 0.8

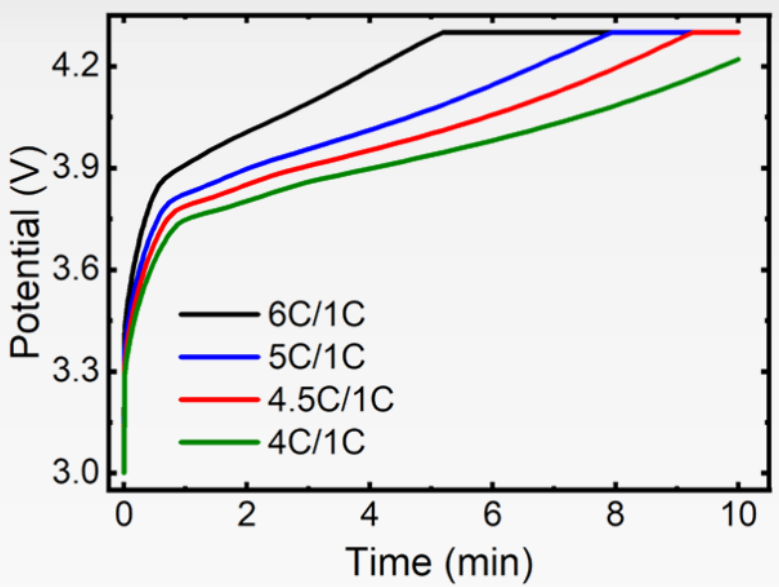
Technical Accomplishment – Impedance of metal-coated electrodes

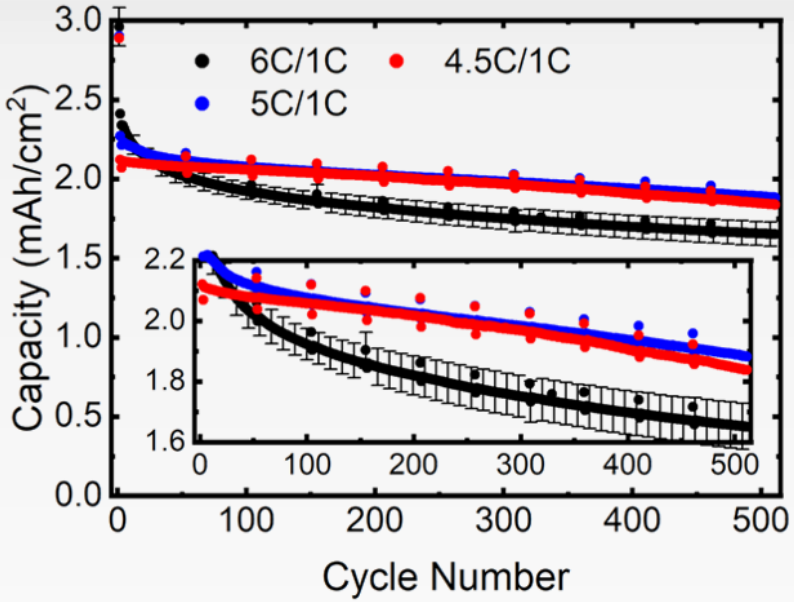


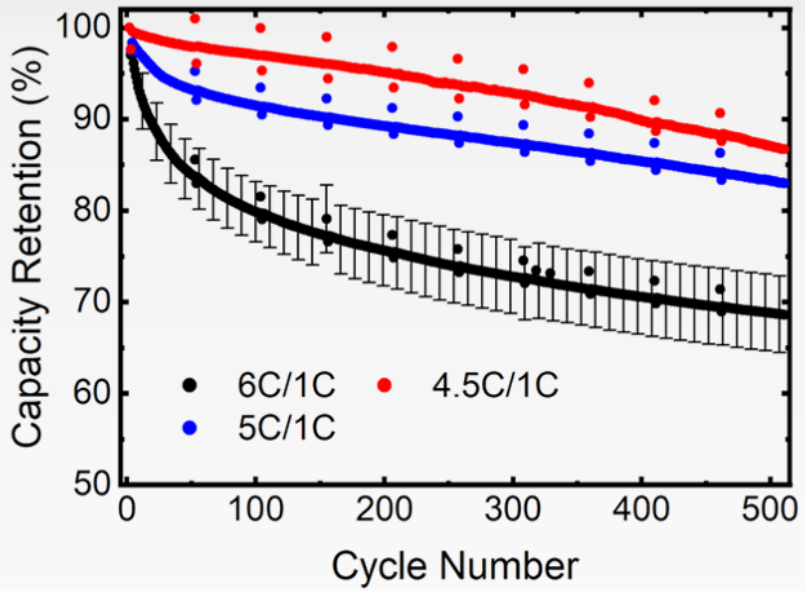
- Impedance of representative cells before and after cycling demonstrate similar profiles independent of metal coating type and thickness

Technical Accomplishment – Optimization of Charging Protocol (constant current)

First 10 min charge



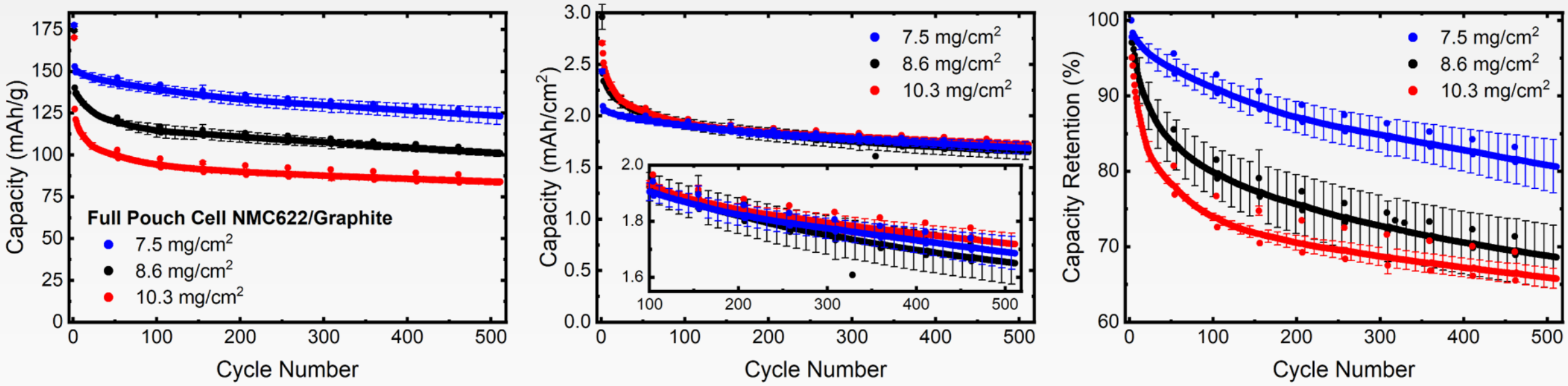




- Optimization of constant current during 10 minute fast charge (CC, CV) protocol was investigated to improve cycling performance of pouch cells
- 5C and 4.5C constant current prolong CC step and result in improved capacity retention when tested at 30°C with 4.3 V voltage cutoff

Technical Accomplishment – Optimization of Anode Loading

10 minute charge, 1C discharge



- Optimization of anode areal loading was performed to maximize specific energy of pouch cells
- Areal loadings greater than 7.5 mg/cm^2 do not increase areal capacity and thus reduce specific energy under fast charging conditions